

DESIGNING OF THE CALCINATION UNIT: TEMPERATURE AND ENERGY PROFILE

SUNIL G. SHINGADE* & PRASHANT D. GANGAWANE

Institute of Chemical Technology, Matunga, Mumbai, India

ABSTRACT

Calcination is the process of thermal decomposition which generally occurs at high temperature below the melting point of the material. The case study of the calcination of calcium oxalate monohydrate has been taken into consideration to predict out the temperature and energy profile of the calcining material along the length of calciner.

KEYWORDS: *Calcination, temperature profile, energy profile, calcium oxalate monohydrate etc.*

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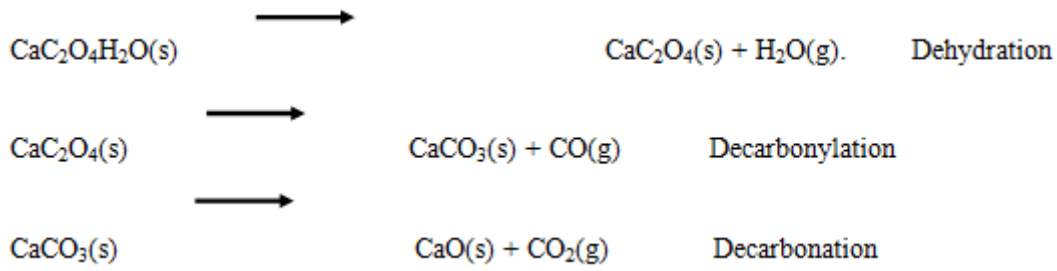
1. INTRODUCTION

Calcination

Calcination is a thermal treatment process in presence of air applied to ores and other solid materials to bring about a thermal decomposition, phase transition, or the removal of volatile fraction. The calcination process normally occurs at temperatures below the melting point of the product materials. Calcium nitrate reacts with oxalic acid in aqueous condition and forms calcium oxalate monohydrate and its subsequent calcination converts it into calcium oxide. Calcium oxide is considered as a crucial ingredient in modern cement and it is going to manufacture from the calcination of calcium oxalate. Calcium oxide can also be used as a chemical flux in smelting. Carbon dioxide generally going to release from the industrial calcination processes and makes it a major contributor to climate change. A calciner is of a cylindrical shape made from steel and it rotates inside the heated furnace. The temperature inside the furnace for carrying out the calcination of calcium oxalate monohydrate to calcium oxide lies in the range of 200 to 900°C. Continuous rotary calcination is a widely used process in which particles flow through a rotating drum having contact with heated walls. Therefore, there is a need for a fundamental understanding of the effects of operation, design, and material properties on the residence time and temperature distributions in the rotary calcination process to provide a methodology for scale-up. For achieving successful calcination, the residence time of particles in the calciner must be longer than the heating and carrying out the actual calcination of the particles (Emady et al; 2013). Calcination of calcium oxalate monohydrate to calcium oxide takes place through multiple steps and hence it is necessary to find out the temperature and energy profile of the calcination material inside the calciner.

2. CALCINATION OF CALCIUM OXALATE MONOHYDRATE

Calcium oxide gets formed through the calcination of calcium oxalate monohydrate. Calcination of calcium oxalate monohydrate takes place through the following steps (Vlaev et al; 2008).



It has been observed that dehydration, decarbonylation and decarbonation takes place at 200, 500 and 850°C respectively. The summation of the heat duties required for all these steps is the total heat duty required for carrying out the calcination of calcium oxalate monohydrate to calcium oxide.

3. ESTIMATION OF HEAT DUTY REQUIRED FOR CARRYING OUT THE CALCINATION OF CALCIUM OXALATE MONOHYDRATE

Heat duty of any reaction can be estimated as follow:

$$\Delta H_{\text{Reaction}} = \Delta H_{f,\text{product}} - \Delta H_{f,\text{reactant}} + \int_{T_{\text{ref}}}^{T_{\text{reaction}}} C_{p,\text{product}} dT - \int_{T_{\text{ref}}}^{T_{\text{reaction}}} C_{p,\text{reactant}} dT \quad (1)$$

The heat of formation (ΔH_f) and heat capacities (C_p) of the reactants and products are required to estimate the heat duty of the reaction. The heat of formation and heat capacities of the reactants and products involved in the calcination of calcium oxalate monohydrate has been tabulated in Table-1.

Table 1: Heat of formation and specific heat of the compounds involved in the calcination of calcium oxalate monohydrate (Yaws; 1999).

Compound	Heat of formation (ΔH_f) (Cal/mol)	Specific heat (C_p) (Cal/molK)
$\text{CaC}_2\text{O}_4\text{H}_2\text{O(s)}$	-399856.597	36.418
$\text{H}_2\text{O(g)}$	-57795.889	$8.22+0.00015T+0.00000134T^2$
$\text{CaC}_2\text{O}_4\text{(s)}$	-332695.985	36.418
CO(g)	-26416.109	$6.60+0.0012T$
$\text{CaCO}_3\text{(s)}$	-288479.924	$19.68+0.01189T-307600/T^2$
CaO(s)	-151790.153	$10+0.00484T-108000/T^2$
$\text{CO}_2\text{(g)}$	-94050.908	$0.34+0.00274T-195500/T^2$

Table 2: The Temperature of Calcination Reactions of Calcium Oxalate Monohydrate (Vlaev et al; 2008)

Reaction	Reaction Name	Decomposition Temperature ($^{\circ}\text{C}$)
$\text{CaC}_2\text{O}_4\text{H}_2\text{O}(\text{s})$ \downarrow $\text{CaC}_2\text{O}_4(\text{s}) + \text{H}_2\text{O}(\text{g})$	Dehydration	200
$\text{CaC}_2\text{O}_4(\text{s})$ \downarrow $\text{CaCO}_3(\text{s}) + \text{CO}(\text{g})$	Decarbonylation	500
$\text{CaCO}_3(\text{s})$ \downarrow $\text{CaO}(\text{s}) + \text{CO}_2(\text{g})$	Decarbonation	850

The heat duty of calcination reactions of calcium oxalate monohydrate has been estimated and tabulated in Table-3.

Table 3: Heat Duty of Calcination Reactions of Calcium Oxalate Monohydrate

Reaction	Reaction Name	Heat duty (Kcal/mol)
$\text{CaC}_2\text{O}_4\text{H}_2\text{O}(\text{s})$ \downarrow $\text{CaC}_2\text{O}_4(\text{s}) + \text{H}_2\text{O}(\text{g})$	Dehydration	17 - 18
$\text{CaC}_2\text{O}_4(\text{s})$ \downarrow $\text{CaCO}_3(\text{s}) + \text{CO}(\text{g})$	Decarbonylation	27 - 28
$\text{CaCO}_3(\text{s})$ \downarrow $\text{CaO}(\text{s}) + \text{CO}_2(\text{g})$	Decarbonation	52

Calcination of calcium oxalate monohydrate takes place in three steps. The first step occurs at 200°C at which water gets separated from calcium oxalate and it is called as dehydration. The second step occurs at 500°C at which carbon monoxide get released and calcium carbonate gets form. This step is called as decarbonylation. The third step occurs at 850°C at which carbon dioxide get released and calcium oxide gets form. This step is known as decarbonation. The heat duty required for carrying out the calcination has been estimated by equation-1. Graphical representation of the reaction heat duty required for each step of the calcination of one mole of calcium oxalate monohydrate has been shown in Figure-1. From the graphical representation, it is clear that sensible heat balance between reactants and products is necessary in order to estimate the heat duty required to raise the temperature of reactants to the temperature at which calcination takes place. For carrying out the first step of calcination, the heat duty of 6.4 kcal is required to raise the temperature of one mole of calcium oxalate monohydrate and its calcination products to 200°C . The additional heat duty of 10.8 kcal is required for

carrying out the conversion of one mole of calcium oxalate monohydrate into calcium oxalate and water at 200°C. For carrying out the second step of calcination, the heat duty of 10.9 kcal is required to raise the temperature of one mole of calcium oxalate and its calcination products to 500°C. Additional heat duty of 17 kcal is required to convert one mole of calcium oxalate into calcium carbonate and carbon monoxide at 500°C. For carrying out the third step of calcination, the heat duty of 10.7 kcal is required to raise the temperature of one mole of calcium carbonate and its calcination products to 850°C. Additional heat duty of 41.44 kcal is required to convert one mole of calcium carbonate into calcium oxide and carbon dioxide at the calcination temperature of 850°C. Total heat duty of 98 kcal is required for carrying out calcination of one mole of calcium oxalate monohydrate to calcium oxide.

4. DESIGNING OF CALCINATION UNIT

Consider the input feed rate of calcium oxalate monohydrate of 30 gm/min is given to the calcination unit. The heat duty required for carrying out the calcination of one mole of calcium oxalate monohydrate (146 gm) has been represented in Figure-1 and on that basis, the heat duty required for carrying out calcination of 30 gm of calcium oxalate monohydrate to calcium oxide has been estimated and represented graphically in Figure-2. Consider a calciner is of a cylindrical shape made from a stainless steel 304 and it rotates inside the heated furnace. Consider the temperature of the inner surface of the calciner is of 900°C throughout the overall length of the calciner. At such a high temperature heat is going to transfer from steel body to the calcining material by radiation. The heat going to emit from the stainless steel surface by radiation per minute is given by Stefan-Boltzmann law as follow:

$$Q = \varepsilon \sigma A(T_s^4)(60) \quad (2)$$

Where ε is the emissivity, σ is the Stefan-Boltzmann constant and it is $5.67 \times 10^{-8} \text{ (W/m}^2\text{K}^4\text{)}$, A is the surface area and T_s is the surface temperature in kelvin. The emissivity of steel surface is of 0.36 (https://www.transmetra.ch/images/transmetra_pdf/publikationen_literatur/pyrometrie-thermografie/emissivity_table.pdf). The heat radiated from the hot steel surface is going to absorb by the calcining material. As the calcining material is white in colour and then its absorptivity is of 0.16 (https://en.wikipedia.org/wiki/Kirchhoff%27s_law_of_thermal_radiation). From Figure-2, it is clear that the heat duty (ΔH_1) of 5481 J is required to raise the temperature of 30 gm of the calcium oxalate monohydrate from 25 to 200°C and it can be achieved in the time period of 60 seconds. The energy balance equation is given by

$$\varepsilon \sigma A(T_s^4)(60)(a) = 5481 \quad (3)$$

Where $A = \pi DL$ and a is the absorptivity of calcining material.

Assume, D is of 10 cm (0.1m) then the estimated length (L) is 5 cm. It means that the material entered per minute inside the calciner has to pass through the rotating calciner adhered to the steel surface along the axis length of 5 cm in one minute then its temperature rises from 25 to 200°C. Similarly, the length of calciner needed for other heat duties (ΔH_2 to ΔH_6) has been estimated. The temperature and energy profile of the calcining material along the length of the calciner has been shown schematically in Figure-3.

CONCLUSIONS

The calcination of calcium oxalate monohydrate to calcium oxide takes place through three steps like dehydration, decarbonylation and decarbonation. These three steps take place at 200, 500 and 850°C respectively. The entire heat duty

of 98 kcal (410032 J) is required for carrying out the calcination of one mole of calcium oxalate monohydrate to calcium oxide. The designing of continuous calciner has been proposed by considering the input feed rate of calcium oxalate monohydrate of about 30 gm/min. The entire heat duty required for carrying the calcination of the calcium oxalate monohydrate entering the calciner to the calcium oxide has been estimated on the basis of the heat duty required for carrying out the calcination of one mole of calcium oxalate monohydrate and it is around 83597 J. The energy and temperature profile of calcining material has been shown graphically. The sizing of continuous cylindrical calciner for carrying out the calcination of incoming feed of calcium oxalate monohydrate to calcium oxide has been done and the temperature and energy profile of the calcining material along with the length of the calciner has been shown schematically.

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Figure-1: Graphical representation of the heat duty required for the calcination of calcium oxalate monohydrate.

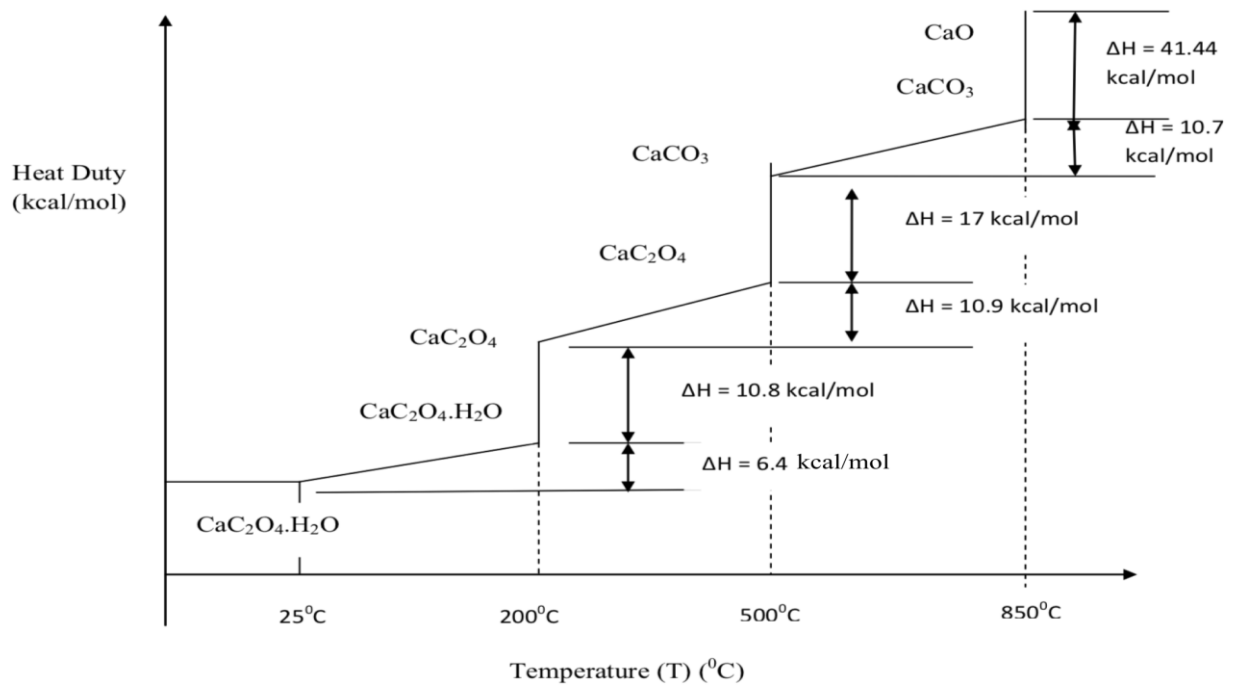


Figure-2: Temperature and Energy profile of calcination material at the input feed rate of 30 gm/min

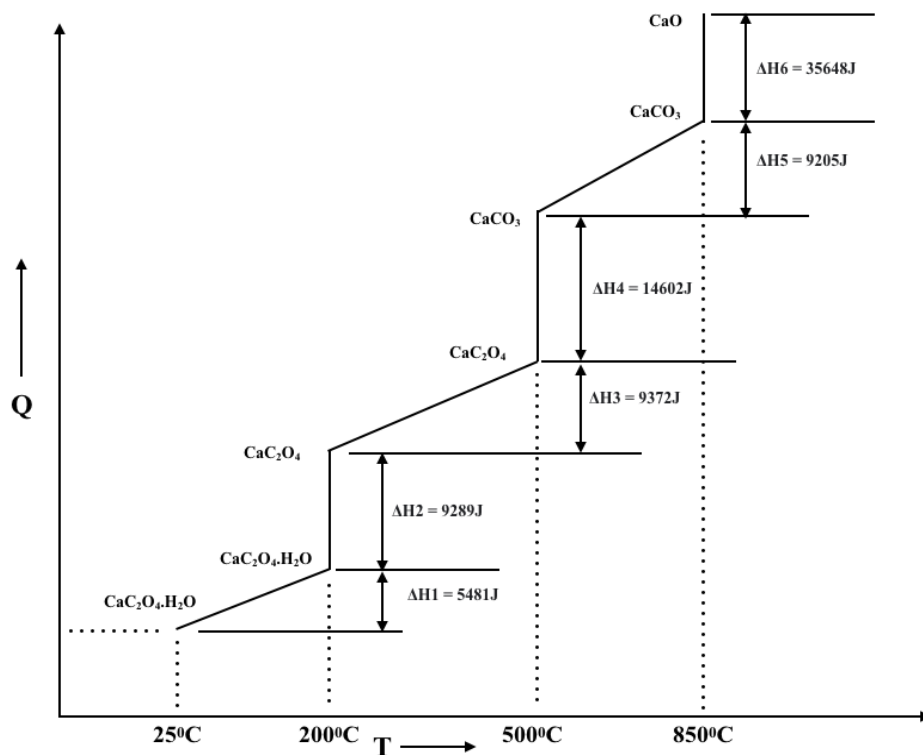
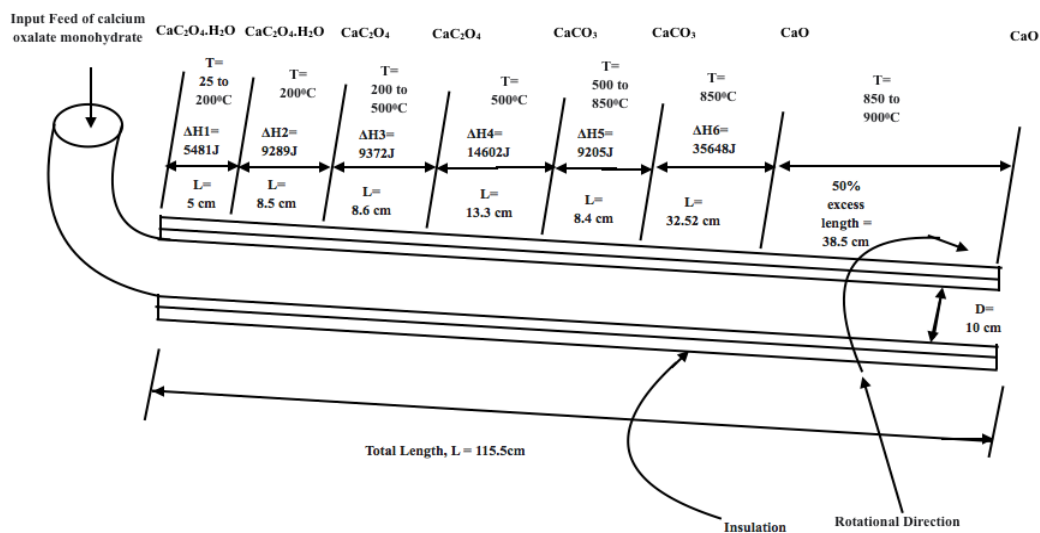


Figure-3: Energy and Temperature profile of calcination material along the length of the calciner



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AUTHOR CONTRIBUTION

S. G. Shingade and P. D. Gangawane studied the calcination operation. S. G. Shingade estimated the heat duty required for carrying out the calcination of calcium oxalate monohydrate to calcium oxide and represented it graphically. S. G. Shingade proposed the designing of continuous calciner along with the prediction of temperature and energy profile of the calcining material across the length of the calciner. Both authors S. G. Shingade and P. D. Gangawane co-wrote the article.

COMPETING INTEREST

Authors declare that don't have any financial competing interest.